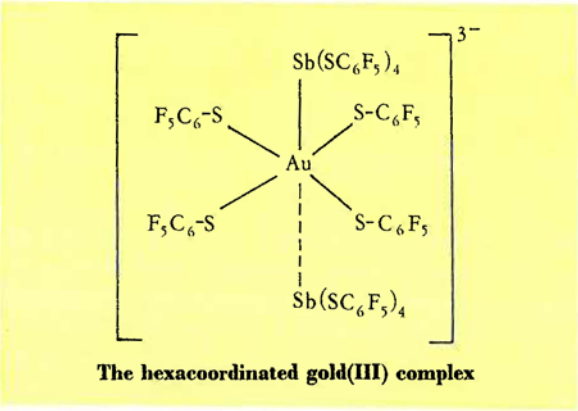



**The hexacoordinated gold(III) complex**

In view of the physical data obtained on these compounds it is not possible to assign them a more detailed structure. In solution, there occurs the complete dissociation:

$$[AuX_4(SbX_4)_2]^{3-} \rightarrow [AuX_4(SbX_4)]^{2-} + SbX_4^-$$

so that the complex anion is now a five-coordinated gold(III) species containing only one Au-Sb bond.

The Au-Sb bonds in compounds (a), (b) and (c) are essentially characterised by their infra-red and Raman stretching frequencies:

$\nu$(Au-Sb) = 181 $cm^{-1}$ in (a), 187 $cm^{-1}$ in (b) and 191 $cm^{-1}$ in (c)

The gold-antimony systems seem to be potential homogeneous catalysts for the hydrogenation of olefins. Indeed, ethylene is hydrogenated to ethane by a deep red ethanolic solution of $HAuCl_4$ or $HAuX_4$ ($\sim 10^{-3}$M) and $SbX_3$ taken in large excess ($\sim 10^{-2}$M) at 0°C and 1 atmosphere total hydrogen pressure. It is necessary to operate with rigorously deoxygenated ethanol and at low temperature, otherwise precipitates are formed and gold metal tends to deposit. A more detailed study of these catalytic properties is under progress.

Thus by using the strong $\pi$-electron withdrawing ligand $X^- = C_6F_5S^-$ in place of the chloride ion it is possible to obtain gold(III)-to-antimony bonded complexes which are the only known antimony analogues of the chlorotin-platinum(II) derivatives and which seem to exhibit the same catalytic properties in the homogeneous hydrogenation of olefins.

### References


1 J. F. Young, *Adv. Inorg. Chem. Radiochem.*, 1968, **11**, 92; E. H. Brooks and R. J. Cross, *Organometal. Chem. Rev.* (*A*), 1970, **6**, 227

2 R. Ugo, Aspects of Homogeneous Catalysis, C. Manfredi ed., Milan, 1970. See pp. 15–24 and the references therein; G. N. Schrauzer, Transition Metals in Homogeneous Catalysis, Marcel Dekker, 1971

3 J. F. Young, R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, 1964, 5176; R. V. Lindsey, G. W. Parshall and U. G. Stolberg, *J. Am. Chem. Soc.*, 1965, **87**, 658; G. W. Parshall, *J. Am. Chem. Soc.*, 1966, **88**, 704

4 H. A. Tayim and J. C. Bailar, *J. Am. Chem. Soc.*, 1967, **89**, 4330

5 R. Cramer and R. V. Lindsey, *J. Am. Chem. Soc.*, 1966, **88**, 3534

6 J. A. Dilts and M. P. Johnson, *Inorg. Chem.*, 1966, **5**, 2079; F. Glocking and M. D. Wilbey, *J. Chem. Soc.* (*A*), 1968, 2168

7 L. Malatesta, L. Naldini, G. Simonetta, and F. Cariati, *Coord. Chem. Rev.*, 1966, **1**, 255

8 W. R. Cullen, D. J. Patmore and J. R. Sams, *Inorg. Chem.*, 1973, **12**, 867 and references therein

9 M. C. Muller, R. J. H. Clark and R. S. Nyholm, submitted for publication

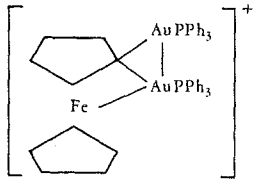
10 W. Beck, K. H. Stetter, S. Tadros, and K. E. Schwarzhans, *Chem. Ber.*, 1967, **100**, 3944; W. Beck and S. Tadros, *Zeit. Anorg. Allgem. Chem.*, 1970, **375**, 231; R. S. Nyholm, J. F. Skinner and M. H. B. Stiddard, *J. Chem. Soc.* (*A*), 1968, 38; B. R. Hollebone and R. S. Nyholm, *J. Chem. Soc.* (*A*), 1971, 332; M. E. Peach, *Canad. J. Chem.*, 1968, **46**, 2699


# New Organometallic Compounds with a Gold-Gold Bond

A new series of organogold compounds has been synthesised in which there are two gold atoms per molecule bonded with one another directly. These have the general formula $[R(AuPPh_3)_2]^+[BF_4]^-$, where $R = C_6H_5$, $p$-$CH_3C_6H_4$, $C_5H_5FeC_5H_4$, and derivatives such as $C_5H_5FeC_5H_3OCH_3$.

These complexes, reported by A. N. Nesmeyanov, E. G. Perebalova, K. I. Grandberg, D. A. Lemenovskii, T. V. Baukova and O. B. Afanasova of the Moscow University Department of Organic Chemistry (*Vest. Moskov. Univ., Ser. II, Khim.*, 1973, **14**, (4), 387–399), are obtained when $^+AuPPh_3$ is generated in the presence of $RAuPPh_3$. An example is the reaction of $HBF_4$ with ferrocenyltriphenylphosphinegold $C_5H_5FeC_5H_4AuPPh_3$, which gives $[C_5H_5FeC_5H_4(AuPPh_3)_2]^+[BF_4]^-$.

The structure of these complexes has been investigated by nuclear magnetic resonance, infra-red and ultra-violet spectroscopy, and in the case of the ferrocenyl complex by X-ray crystallography (V. G. Andrianov, Yu. T. Struchkov and E. R. Rosinskaya, *J. Chem. Soc., Chem. Commun.*, 1973, 338). This is the first X-ray study on a ferrocene derivative with a direct iron-to-metal bond and the structure is as shown here. It is also the first known example of a cyclopentadienyl ring bridging (*exclusively* through one of its carbon atoms) *two* metal (Au) atoms.




These compounds undergo two main types of reaction involving either one or both of the $AuPPh_3$ groups.

An example of the first type is the reaction of $PPh_3$ with the $p$-tolyl complex (i.e. $R = p$-$CH_3C_6H_4$), which gives $[Ph_3PAuPPh_3]^+$ and $CH_3C_6H_4AuPPh_3$. The relative stabilities of ions of the general formula $[LAuPPh_3]^+$ is discussed for a number of ligands L. The second type involves reaction with other organometallic complexes and results in the interchange of organic radicals.

C. W. B.